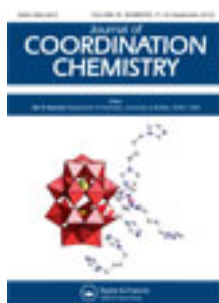


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Synthesis, crystal structures, and infrared spectroscopy of a series of lanthanide phosphonoacetate coordination polymers

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Hydrothermal reactions of lanthanide chloride, phosphonoacetic acid ($\text{H}_2\text{O}_3\text{PCH}_2\text{COOH}$), and water in the presence of HCl provide a series of lanthanide coordination polymers. FT-IR spectra confirm that there are three kinds of structures among seven complexes, $\{[\text{Ln}_2(\text{O}_3\text{PCH}_2\text{CO}_2)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}\}_\infty$ (type I) ($\text{Ln} = \text{La}^{\text{III}}$ for 1; Pr^{III} for 2; Nd^{III} for 3 and Eu^{III} for 4), $[\text{Ln}(\text{O}_3\text{PCH}_2\text{CO}_2)(\text{H}_2\text{O})_2]_\infty$ (type II) ($\text{Ln} = \text{Tb}^{\text{III}}$ for 5), and $[\text{Ln}(\text{O}_3\text{PCH}_2\text{CO}_2)(\text{H}_2\text{O})_2]_\infty$ (type III) ($\text{Ln} = \text{Ho}^{\text{III}}$ for 6 and Yb^{III} for 7). Complexes 1–5 show 2-D 4,4,5,5-connected $(4^4 \cdot 6^2)(4^5 \cdot 6)(4^6 \cdot 6^4)(4^8 \cdot 6^2)$ topology networks and 2-D 4-connected $(4^4 \cdot 6^2)$ topology networks and then are further linked into 3-D supramolecular networks by hydrogen-bonding interactions; 6 and 7 both exhibit a 3-D 4-connected $(4^2 \cdot 6^3 \cdot 8)$ topology with 1-D dumbbell-shaped channels. The results indicate infrared spectroscopy is in accord with the result of single-crystal X-ray analysis.

Keywords: Phosphonoacetic acid; Lanthanide complexes; Infrared spectra; Crystal structures

1. Introduction

There is increasing interest in the design and synthesis of metal–organic frameworks due to structural diversity [1] and potential applications in molecular adsorption and separation processes [2], gas storage [2, 3], ion exchange [4], catalysis [5], sensor technology [6], etc. Formation of these complexes mainly depends on coordination geometry of metal ions and the nature of ligands [7]. Choice of ligands favoring structure-specific self-assembly is crucial for construction of coordination structures with relevant properties and functions [8]. Among various ligands, carboxylic acids [2b, 9] and phosphonic acids [10] have been used in preparation of various complexes owing to their rich coordination modes.

Phosphonoacetates with carboxylic acid groups and phosphonic acid groups are remarkably versatile building blocks for assembling extended structures [11]. Lanthanides tend to coordinate with the O-donors in high and flexible coordination numbers compared with transition metal ions [12]. Few lanthanide complexes containing phosphonoacetate ligands have been reported [13]. Besides coordination bonds [14], weak intra- or intermolecular interactions, such as hydrogen bonds [15]

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from coordinated and free water molecules [16], also affect final structures of such complexes and may link discrete subunits or low-dimensional entities into higher dimensional supramolecular networks [17].

To systematically investigate relationships between lanthanide ions and their phosphonoacetic complexes, we synthesized and characterized seven lanthanide phosphonoacetate $[(O_3PCH_2COO)^{3-}]$ complexes by infrared spectra and single-crystal X-ray diffraction analyses.

2. Experimental

2.1. Materials and general methods

All chemicals were analytically pure (>99.99%) and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 C analyzer. IR spectra were obtained with a Varian Scimitar Series 800 FT-IR spectrometer at resolution of 4 cm^{-1} and 32 scans in the $400\text{--}4000\text{ cm}^{-1}$ region on pressed KBr pellets.

2.2. Syntheses of 1–7

In the presence of hydrochloric acid (HCl , 1 mol L^{-1} , 0.5 mL), a mixture of 0.3 mmol of phosphonoacetic acid ($\text{H}_2\text{O}_3\text{PCH}_2\text{COOH}$) and 0.3 mmol of $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ was dissolved in 10 mL deionized water. The resultant solution was heated at 150°C for 4 days. Corresponding single crystals suitable for X-ray analyses were obtained after cooling to room temperature. After filtering, the product was washed with ethanol and dried under ambient conditions. Yield: $\sim 20\%$ based on $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ for **1**, $\sim 40\%$ based on $\text{PrCl}_3 \cdot 6\text{H}_2\text{O}$ for **2**, $\sim 30\%$ based on $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ for **3**, $\sim 30\%$ based on $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ for **4**, $\sim 20\%$ based on $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ for **5**, $\sim 40\%$ based on $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ for **6**, $\sim 20\%$ based on $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ for **7**. For **1**, Anal. Calcd for $\text{C}_4\text{H}_{12}\text{La}_2\text{P}_2\text{O}_{14}$: C, 7.69; H, 1.94; Found (%): C, 7.95; H, 1.69. For **2**, Anal. Calcd for $\text{C}_4\text{H}_{12}\text{Pr}_2\text{P}_2\text{O}_{14}$: C, 7.65; H, 1.93; Found (%): C, 7.40; H, 2.14. For **3**, Anal. Calcd for $\text{C}_4\text{H}_{12}\text{Nd}_2\text{P}_2\text{O}_{14}$: C, 7.62; H, 1.92; Found (%): C, 7.28; H, 2.11. For **4**, Anal. Calcd for $\text{C}_4\text{H}_{12}\text{Eu}_2\text{P}_2\text{O}_{14}$: C, 7.36; H, 1.86; Found (%): C, 7.68; H, 1.44. For **5**, Anal. Calcd for $\text{C}_2\text{H}_6\text{PTbO}_7$: C, 7.23; H, 1.82; Found (%): C, 7.43; H, 1.54. For **6**, Anal. Calcd for $\text{C}_2\text{H}_6\text{PHoO}_7$: C, 7.10; H, 1.79; Found (%): C, 7.57; H, 1.33. For **7**, Anal. Calcd for $\text{C}_2\text{H}_6\text{PYbO}_7$: C, 6.92; H, 1.74; Found (%): C, 6.64; H, 1.98.

2.3. Crystal structure determination

Single-crystal X-ray data for **1–7** were collected on a Bruker SMART 1000 CCD diffractometer equipped with graphite monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) by ω scan mode. SAINT [18] was used for integration of the diffraction profiles. All structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares with SHELXL (semi-empirical absorption corrections were applied using SADABS) [19]. Positions of the metal atoms were located from the E -map by direct-methods, other non-hydrogen

Table 1. Crystal data and structure refinement summary for 4–7.

	4	5	6	7
Empirical formula	C ₄ H ₁₂ Eu ₂ P ₂ O ₁₄	C ₂ H ₆ PTbO ₇	C ₂ H ₆ PHoO ₇	C ₂ H ₆ PYbO ₇
Formula weight	650.00	331.96	337.97	346.08
Crystal system	Triclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 1	<i>P</i> 21/ <i>c</i>	<i>Pnma</i>	<i>Pnma</i>
Unit cell dimensions (Å, °)				
<i>a</i>	8.856(2)	8.6371(14)	13.086(3)	15.220(2)
<i>b</i>	8.867(2)	9.4247(15)	6.8381(15)	6.7786(10)
<i>c</i>	9.676(2)	9.1995(14)	7.7977(17)	7.1846(11)
α	109.675(2)	90	90	90
β	107.449(2)	108.115(2)	90	90
γ	91.961(3)	90	90	90
Volume (Å ³), <i>Z</i>	674.8(3), 2	711.74(19), 4	697.8(3), 4	741.23(19), 4
Calculated density (g cm ⁻³)	3.199	3.098	3.217	3.101
Absorption coefficient (mm ⁻¹)	9.522	10.152	11.559	12.824
<i>F</i> (000)	608	616	624	636
Collected reflections	4827	4578	5016	5269
Unique reflections	2443	1322	711	747
<i>R</i> _{int}	0.0450	0.0329	0.0264	0.0308
Goodness-of-fit on <i>F</i> ²	1.013	1.020	1.047	1.039
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0388	0.0216	0.0139	0.0176
<i>wR</i> ₂ (all data) ^b	0.0819	0.0445	0.0328	0.0486
ρ_{\max} and ρ_{\min} (e Å ⁻³)	1.354 and -1.388	0.674 and -0.755	0.474 and -1.086	0.973 and -0.841

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

atoms were located in difference Fourier syntheses and least-squares refinement cycles, and finally refined anisotropically. Hydrogen atoms of the ligands were placed theoretically onto specific atoms and refined isotropically as riding mode. Crystallographic data and experimental details for structural analyses are summarized in table 1. Selected bond lengths and angles are listed in table S1.

3. Results and discussion

3.1. Infrared spectroscopy

Infrared spectroscopy provides a method for studying crystalline compounds, as infrared modes are sensitive to changes in bond angles [20]. The seven complexes can be divided into three types according to their infrared spectra (figure 1). Type I includes complexes formed by La^{III}, Pr^{III}, Nd^{III}, and Eu^{III}, which belongs to the lighter elements among lanthanides, and usually have higher coordination numbers. Type II includes one complex formed by Tb^{III}, which belongs to middle elements among lanthanides. Type III includes two complexes formed by Ho^{III} and Yb^{III}, heavier lanthanides, which usually have lower coordination numbers.

Infrared spectra of the complexes are characterized by strong bands at 990–1150 cm⁻¹ attributed to ν (P–O) of phosphonoacetate [(O₃PCH₂COO)³⁻] and strong bands at 1350–1650 cm⁻¹ associated with ν (O–C–O)⁻ of phosphonoacetate [21]. Infrared spectra of isostructural complexes are similar because the attached cation

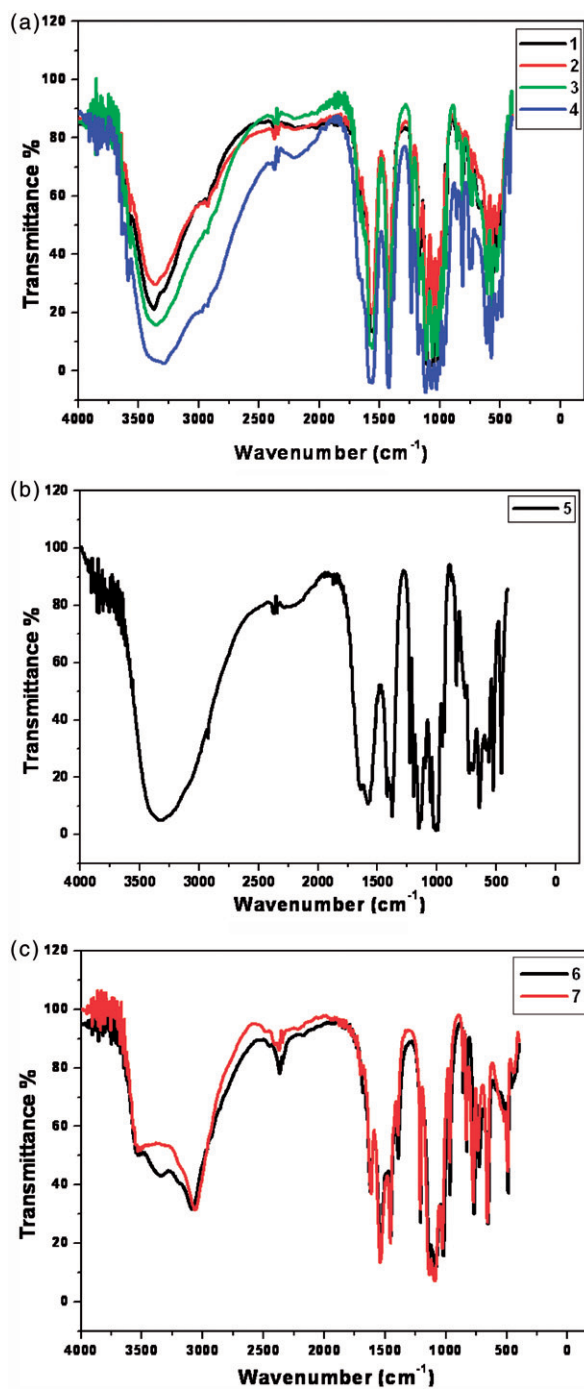


Figure 1. Infrared spectra of (a) 1–4; (b) 5; (c) 6 and 7.

generally has only a small effect on the wavenumber of the complex anion. Among the complexes of the same type, the corresponding vibration frequencies of phosphonate ($-\text{PO}_3^{2-}$) and carboxylate ($-\text{CO}_2^-$) are very similar. For example, in type I the P–O stretching bands are at 1018, 1056, and 1109 cm^{-1} for La^{III} phosphonoacetate (**1**), at 1020, 1059, and 1112 cm^{-1} for Pr^{III} phosphonoacetate (**2**), at 1023, 1062, and 1113 cm^{-1} for Nd^{III} phosphonoacetate (**3**), and at 1029, 1070, and 1118 cm^{-1} for Eu^{III} phosphonoacetate (**4**) (figure 1a).

In a crystalline compound, water molecules produce characteristic bands at 3700–2900 and 1700–1600 cm^{-1} , due to O–H stretch and bend, respectively [22]. As shown in figure 1, similar infrared spectra bands of water show that water molecules have similar lattice environments.

3.2. Description of single-crystal X-ray structures

As expected, based on the infrared spectra of the complexes, **4** is isostructural with **1–3**, which have been reported [13g], and **7** is isostructural with **6**. The structures of **4–7** will be discussed in detail.

3.2.1. $\{[\text{Eu}_2(\text{O}_3\text{PCH}_2\text{CO}_2)_2(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}\}_\infty$ (4**).** Similar to **1–3** [13g], **4** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit consists of two Eu^{III} ions, two phosphonoacetates, three coordinated water molecules, and one free water molecule (figure 2a). Eu(1) is nine-coordinate by one carboxylate oxygen atom and one phosphonate oxygen atom from one phosphonoacetate ligand in scheme 1(a) mode, two carboxylate oxygen atoms and two phosphonate oxygen atoms from three phosphonoacetate ligands in scheme 1(b) mode, two carboxylate oxygen atoms from one phosphonoacetate ligand in scheme 1(c) mode and one oxygen atom from coordinated water [$\text{Eu}-\text{O} = 2.350(6)–2.736(8) \text{ \AA}$] (table S1) [12, 13e, 23]. Eu(2) is also nine-coordinate by three phosphonate oxygen atoms from two phosphonoacetate ligands in scheme 1(a) mode, one carboxylate oxygen atom and one phosphonate oxygen atom from phosphonoacetate ligand in scheme 1(b) mode, two phosphonate oxygen atoms from one phosphonoacetate ligand in scheme 1(d) mode and two oxygen atoms from two coordinated water molecules [$\text{Eu}-\text{O} = 2.342(7)–2.899(7) \text{ \AA}$] (table S1) [12, 13e, 23]. Eu^{III} ions are connected through phosphonoacetate bridges resulting in 2-D layers. To better describe the overall 2-D coordination polymer, it is best to reduce it to its underlying topological net. Eu(1) and Eu(2) can be regarded as 5-connected and 4-connected nodes, respectively, while the phosphonoacetate_{O1–O4} and phosphonoacetate_{O6–O10} are topologically 5-connected and 4-connected bridges, respectively. Thus a 4,4,5,5-connected 2-D topology network is formed (figure 2b). The Schläfli symbol for this network is $(4^4 \cdot 6^2)(4^5 \cdot 6)(4^6 \cdot 6^4)(4^8 \cdot 6^2)$ [24]. Because of coordinated and lattice water molecules between layers, there are nine kinds of hydrogen-bonding interactions (table 2) [15] linking 2-D layers into a 3-D supramolecular network (figure 2c) [17a, 25].

3.2.2. $[\text{Tb}(\text{O}_3\text{PCH}_2\text{CO}_2)(\text{H}_2\text{O})_2]_\infty$ (5**).** In **5**, Tb^{III} is eight-coordinate by one carboxylate oxygen atom and three phosphonate oxygen atoms from three phosphonoacetate ligands in scheme 1(e) mode, two phosphonate oxygen atoms from one

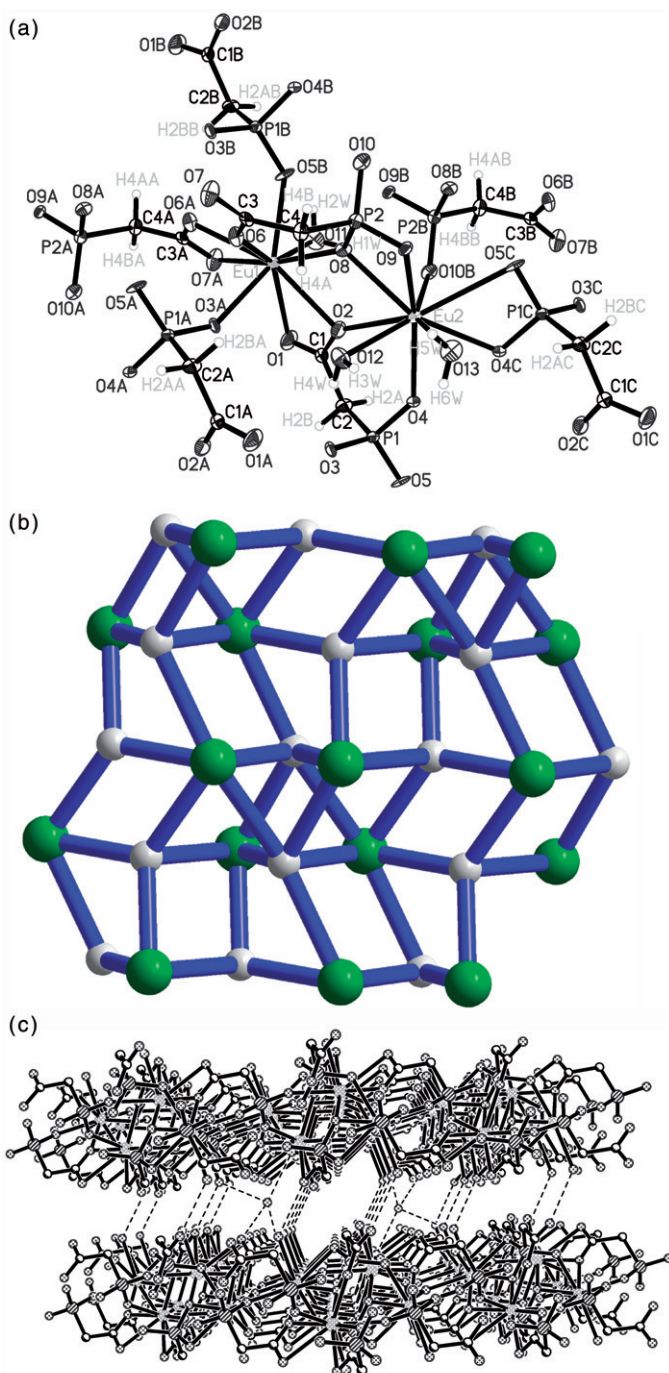
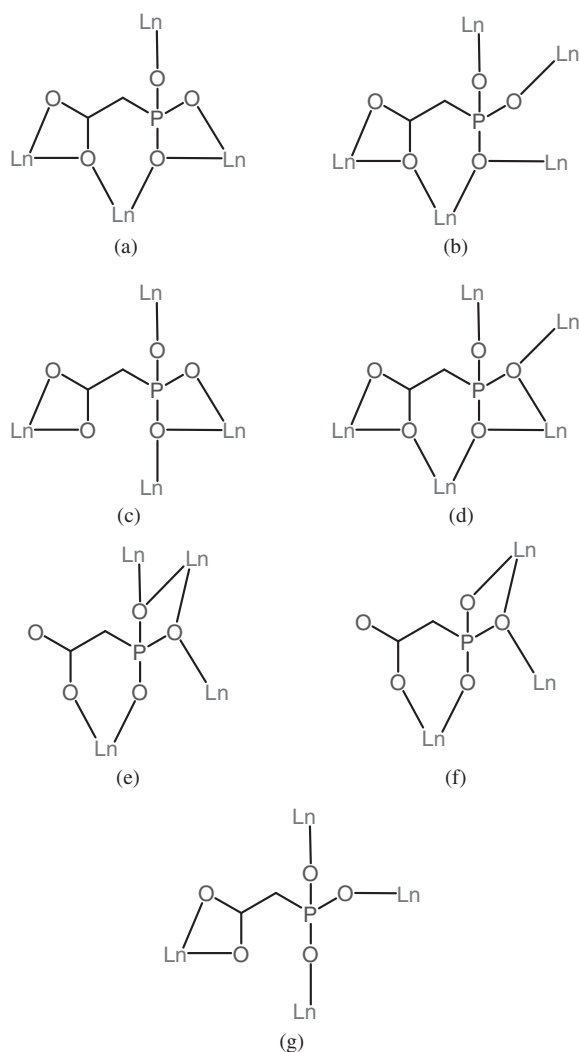


Figure 2. View of (a) the coordination environment of Eu^{III} with 50% thermal ellipsoids in **4**; (b) the 2-D 4,4,5,5-connected $(4^4 \cdot 6^2)(4^5 \cdot 6)(4^6 \cdot 6^4)(4^8 \cdot 6^2)$ topology network, green balls for Eu^{III} ions and white balls for phosphonoacetate; (c) the packing diagram viewed along the c -axis for **4** (some hydrogen atoms omitted for clarity).



Scheme 1. Schematic view of the coordination modes of phosphonoacetate.

phosphonoacetate ligand in scheme 1(f) mode and two oxygen atoms from two coordinated water molecules [Tb–O = 2.248(3)–2.708(3) Å] (table S1) (figure 3a). The average bond length of Tb–O is 2.414 Å, in good agreement with those reported complexes [12, 26]. Tb^{III} connect to adjacent Tb^{III} ions through phosphonoacetate anion bridges resulting in a 2-D layer. Tb^{III} can be regarded as 4-connecting nodes, while the phosphonoacetates also act as topologically 4-connecting, bridging adjacent Tb^{III} ions. Thus a 2-D 4-connected topology network is formed (figure 3b). The Schläfli symbol for this network is (4⁴ · 6²) [24]. The coordinated water molecules can form four kinds of hydrogen-bonding interactions (table 2) [15]. Consequently the 2-D layers further are linked into a 3-D supramolecular network by hydrogen-bonding interactions (figure 3c) [17a, 25].

Table 2. Hydrogen-bonding interaction parameters (\AA , $^\circ$) for **4**, **5**, and **7**.

Complex	D–H	$d(\text{D–H})$	$d(\text{H}\cdots\text{A})$	$\angle\text{DHA}$	$d(\text{D}\cdots\text{A})$	Position of A
4	O(14)–H(8W)	0.83	1.94	160.7	2.736(11)	O(10) $[x, y, z - 1]$
	O(14)–H(7W)	0.83	2.11	130.7	2.729(11)	O(1) $[x + 1, y + 1, z]$
	O(13)–H(6W)	0.83	2.23	122.3	2.762(12)	O(14) $[x - 1, y, z + 1]$
	O(13)–H(5W)	0.83	2.40	115.2	2.848(10)	O(7) $[-x + 1, -y + 1, -z + 2]$
	O(12)–H(4W)	0.83	2.03	167.9	2.847(10)	O(3)
	O(12)–H(3W)	0.83	2.43	116.0	2.894(10)	O(13)
	O(12)–H(3W)	0.83	2.13	133.6	2.765(12)	O(14) $[-x + 1, -y + 1, -z + 1]$
	O(11)–H(2W)	0.86	2.49	116.5	2.873(10)	O(5) $[x + 1, y, z]$
	O(11)–H(1W)	0.85	2.13	117.7	2.632(10)	O(9) $[-x + 1, -y, -z + 2]$
5	O(7)–H(4W)	0.83	2.02	151.8	2.782(6)	O(4) $[-x + 1, y - 1/2, -z + 1/2]$
	O(7)–H(3W)	0.83	1.90	170.7	2.726(6)	O(5) $[x, -y + 3/2, z - 1/2]$
	O(6)–H(2W)	0.83	1.88	149.9	2.628(6)	O(4) $[-x + 1, y - 1/2, -z + 1/2]$
	O(6)–H(1W)	0.83	2.09	166.2	2.898(6)	O(7) $[x, -y + 1/2, z + 1/2]$
7	O(2)–H(2W)	0.83	1.83	168.2	2.640(3)	O(5) $[x, -y + 3/2, z]$
	O(1)–H(1W)	0.88	2.38	128.5	3.008(6)	O(3) $[-x + 3/2, y + 1/2, z + 1/2]$

3.2.3. $[\text{Ho}(\text{O}_3\text{PCH}_2\text{CO}_2)(\text{H}_2\text{O})_2]_\infty$ (**6**) and $[\text{Yb}(\text{O}_3\text{PCH}_2\text{CO}_2)(\text{H}_2\text{O})_2]_\infty$ (**7**).

Complexes **6** and **7** are isostructural except for the metal centers, Ho^{III} for **6** and Yb^{III} for **7**. Here we describe **7** in detail (figure 4). Yb^{III} is seven-coordinate by two carboxylate oxygen atoms and three phosphonate oxygen atoms from four phosphonoacetate ligands in scheme 1(g) mode and two oxygen atoms from two coordinated water molecules [$\text{Yb–O} = 2.131(4)–2.425(3) \text{\AA}$] (table S1) (figure 4a) [27]. The average Yb–O bond length is 2.283\AA , in the expected ranges [12, 27, 28]. Two kinds of hydrogen-bonding interactions are formed by coordinated water (table 2) [15]. Yb^{III} ions are connected by phosphonoacetate anions to form a 3-D open framework with 1-D dumbbell-shaped channels (figure 4c), very similar with $[\text{Zn}(\text{O}_3\text{PCH}_2\text{CO}_2)] \cdot \text{H}_3\text{O}$ [21c], $[\text{Zn}(\text{O}_3\text{PCH}_2\text{CO}_2)] \cdot \text{NH}_4$ [29], and $[\text{Zn}(\text{O}_3\text{PCH}_2\text{C}(\text{O})\text{NH}_2)] \cdot \text{H}_2\text{O}$ [21d]. The Yb^{III} ions can be regarded as four-connecting nodes, while the phosphonoacetates also act as topologically 4-connecting, bridging adjacent Tb^{III} ions with a 3-D 4-connected ($4^2 \cdot 6^3 \cdot 8$) topology formed (figure 4b) [24]. Single-crystal X-ray analyses indicate **6** and **7** have almost the same structure except for metal ions, but compared to **7** there is an additional band at 3345 cm^{-1} in the infrared spectrum of **6** (figure 1c), which can be attributed to O–H stretching of free water attached on the surface of crystals.

Single-crystal X-ray diffraction analyses reveal **1–4** and **6–7** are isostructural, respectively, in agreement with infrared spectroscopic analyses.

4. Conclusion

Seven lanthanide phosphonoacetate complexes have been hydrothermally synthesized and characterized by infrared spectroscopy and single-crystal X-ray analysis. The infrared spectroscopy provides a facile method to judge whether complexes are isostructural and is in accord with single-crystal X-ray analysis. Because of coordinated

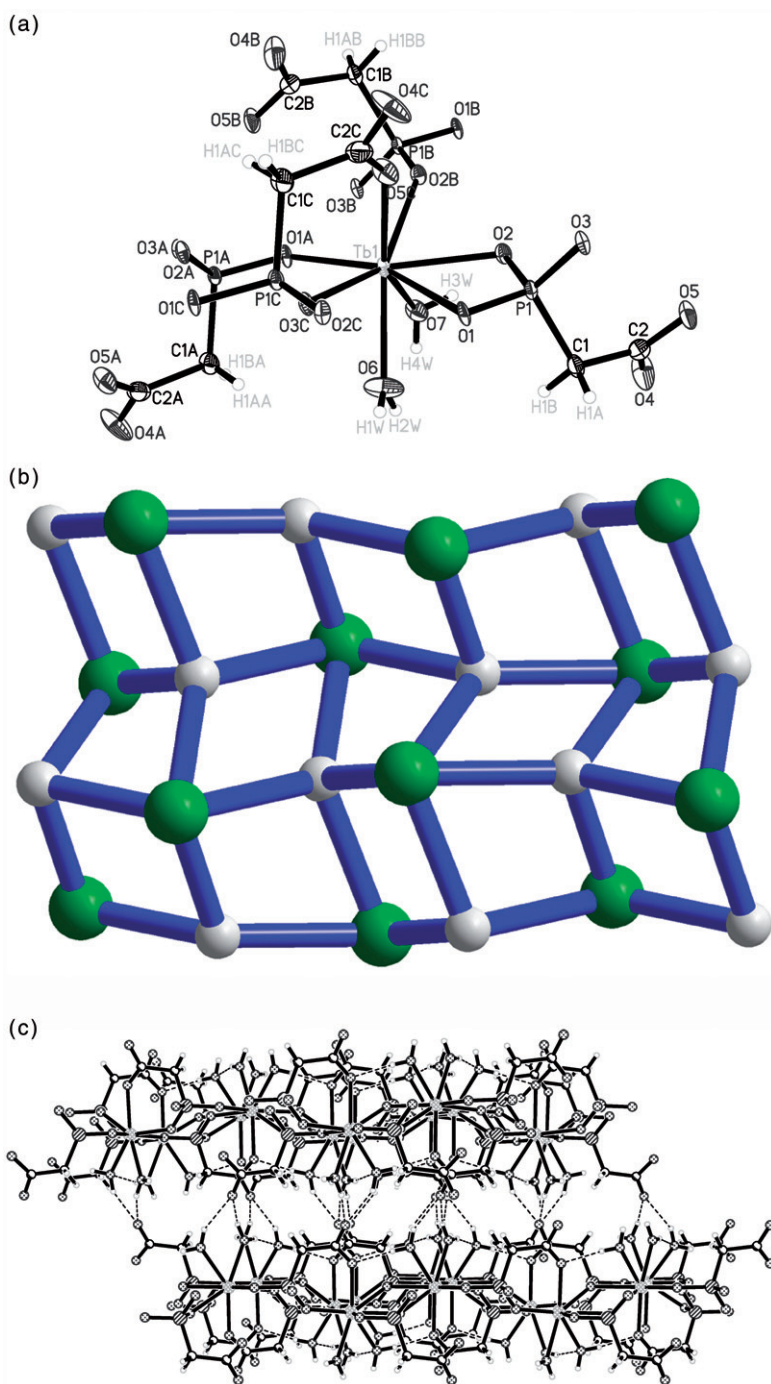


Figure 3. View of (a) the coordination environment of Tb^{III} in **5** (50% thermal ellipsoids); (b) the 2-D 4-connected ($4^4 \cdot 6^2$) topology network, green balls for Tb^{III} and white balls for phosphonoacetate; (c) the packing diagram viewed along the c -axis for **5**.

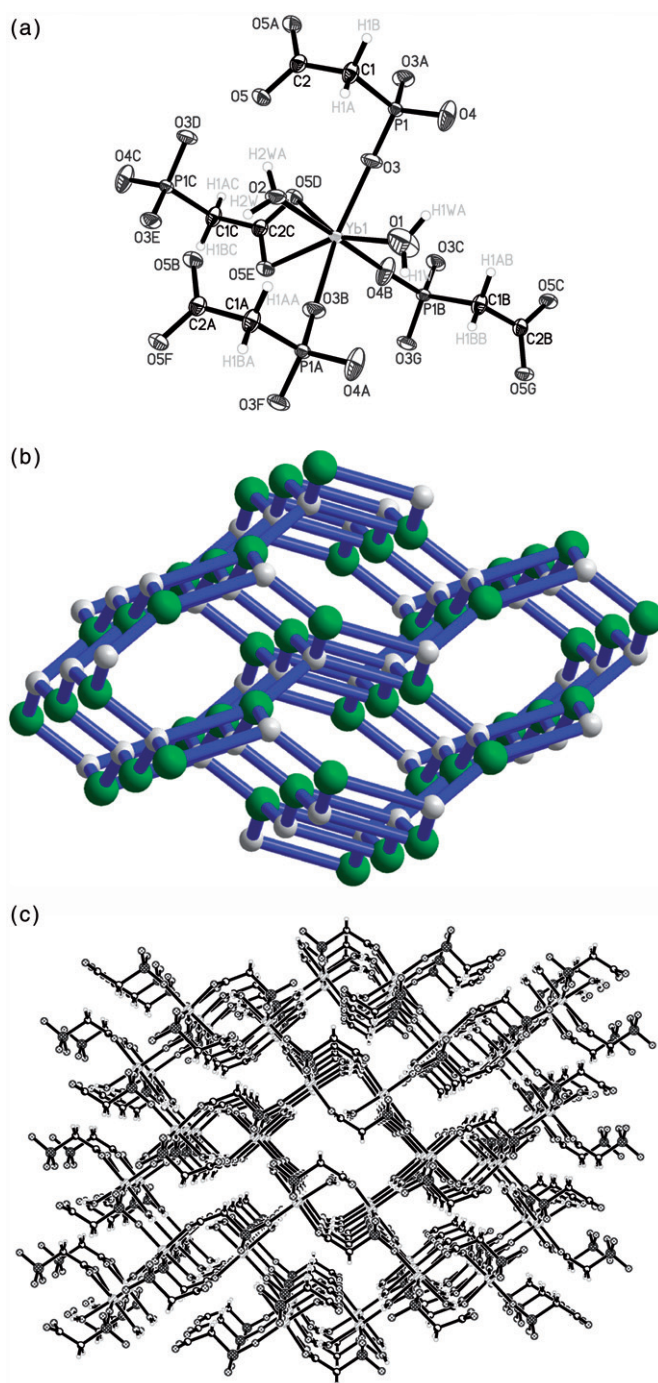


Figure 4. View of (a) the coordination environment of Yb^{III} in 7 (50% thermal ellipsoids); (b) the 4-connected 3-D ($4^2 \cdot 6^3 \cdot 8$) topology network, green balls for Yb^{III} and white balls for phosphonoacetate; (c) the packing diagram viewed along the *b*-axis for 7 (hydrogen-bonding interactions omitted for clarity).

water or lattice water, hydrogen-bonding interactions further link lower dimension structures into a higher dimension supramolecular network.

Supplementary material

Crystallographic data for the crystal structures reported in this article have been deposited with the Cambridge Crystallographic Data Center (CCDC 851914–851917 for 4–7). This material can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223336033; E-mail: deposit@ccdc.cam.ac.uk).

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